

# Emission Control through Catalysis

## CATL 1

### Improve FCC gasoline qualities and clean exhaust gases

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The petroleum refining and automobile industry are networking to solve the environmental problems caused by road transport. Improved fuel qualities and clean exhaust gases are the ongoing aim to further improve air quality in the meantime. In response to ensure a sustainable environment in China, Research Institute of Petroleum Processing has been working on improving fuel qualities and cleaning exhaust gases simultaneously. Results concerning reducing olefin and sulfur content in FCC gasoline, deSOx and progress in automotive catalyst research will be reported in this paper.

## CATL 2

### FTIR Study of the interaction of dioxin, carbazole, dibenzothiophene, and 4,6-dimethyldibenzothiophene on metal oxide catalysts

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Sulphur and nitrogen impurities in gasoil fractions are carried mainly by dibenzothiophenes and carbazoles. Dibenzofurans also carry oxygen impurities and, in particular when chlorided, are formed as gaseous products in incinerators. The destruction of these compounds is obtained by heterogeneously catalyzed technologies, as hydrotreatings (HDN, HDS) or/and on SCR catalysts (for dioxins). However, 4,6-dialkyl benzothiophenes are very resistant to HDS. As a preliminary step of a systematic investigation, we studied the adsorption of dioxin, carbazole, dibenzothiophene and 4,6-dimethyldibenzothiophene over simple metal oxides. Dioxin is bonded to Lewis sites through the oxygen atoms but is very resistant to decomposition. Carbazole is dissociated at its N atom and decomposes quite easily. Dibenzothiophene is also bonded through its S atom while 4,6-dimethyl-dibenzothiophene is very weakly adsorbed probably only through its aromatic electron cloud, due to the steric hindrance on the S atom. MAL thanks MEC for a FPI grant.

## CATL 3

### Ultra deep HDS catalysis in production of clean diesel fuels

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While many believed that HDS chemistry and catalysis were well understood and becoming a minor topic the world-wide trend towards ultra-clean fuel sparked new discussions. The (proposed) new specifications for diesel fuel challenges oil refineries and catalyst manufacturers to fully optimize fuel processing and catalyst performance. Deep knowledge of the underlying chemistry is essential for meeting that challenge. Most interesting, it has become clear that ultra deep HDS is very different from conventional desulfurization. The removal of sterically hindered sulfur species proceeds via different routes, which can be favored by choice of catalyst and reaction conditions. In this paper ultra deep HDS chemistry and catalysis will be discussed together with some intriguing phenomena encountered in commercial application of our deep HDS catalysts.

## Emission Control through Catalysis

### CATL 4

#### **New catalytic materials for hydrodesulfurization catalysis**

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The HDS catalytic properties of oxide-supported metal carbides, nitrides, phosphides and borides have been examined. While Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> and Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalysts are more active than sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, bimetallic Co<sub>3</sub>Mo<sub>3</sub>N/Al<sub>2</sub>O<sub>3</sub> catalysts are less active than sulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts with similar metal loadings. A new, supported bimetallic nitride phase (Ni<sub>2</sub>Mo<sub>3</sub>N/Al<sub>2</sub>O<sub>3</sub>) has been prepared and catalytic results will also be presented for this material. Promoted molybdenum carbide and nitride catalysts exhibit superior HDS catalytic properties compared to conventional sulfide catalysts. For example, Co-Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalysts are as much as 34% higher than sulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts with identical metal loadings. The HDS activities of the bimetallic and promoted carbide and nitride catalysts are strongly dependent upon the pretreatment conditions and this will be discussed in detail. Preliminary results for oxide-supported metal phosphide (e.g. MoP/SiO<sub>2</sub>) and boride (e.g. Ni-B/SiO<sub>2</sub>) catalysts will also be presented.

### CATL 5

#### **Preparation of titania (TiO<sub>2</sub>) catalyst support of a large specific surface by applying the pH swing method for ultra-deep HDS of diesel oil**

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It is widely accepted that specific activity of titania catalyst is superior to alumina catalyst. But, titania (TiO<sub>2</sub>) supported metal catalyst has not been employed, so far, for industrial use in hydrodesulfurization (HDS) or hydrotreating processes, because titania is regarded having a small specific surface area less than 50-60m<sup>2</sup>/g and poor thermal stability. In order to enhance the catalytic performance of TiO<sub>2</sub> supported catalysts for HDS, preparation methods of TiO<sub>2</sub> supports were studied. The technology of the pH swing method realized TiO<sub>2</sub> supports with specific surface area larger than 100m<sup>2</sup>/g and high thermal stability. Furthermore, it was also found that Co-Mo catalyst supported on the TiO<sub>2</sub> supports showed much higher catalyst activities for ultra-deep HDS of diesel oil than conventional commercial HDS catalysts.

### CATL 6

#### **Catalytic decarboxylation of low-rank Turkish Elbistan lignite**

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Decarboxylation of low-rank Turkish Elbistan lignite at low temperatures by utilizing cupric sulphate as catalyst was investigated. The gross calorific value of the lignite treated with 4% (wt) Cu<sup>2+</sup> and decarboxylated at 200°C for 30 minutes increased about 40%. FTIR and solid state <sup>13</sup>C NMR methods have been used to investigate the changes in the oxygen functional groups in Elbistan lignite that occurred during decarboxylation. Activation energies of the decarboxylation reactions were calculated as 100.7 kJ/mol and 44.5 kJ/mol, for original and treated Elbistan lignite samples, respectively. The sequence in the rate of loss of the oxygen functional groups was as carboxyl, carbonyl, hydroxyl, carboxylate ions. With the presence of Cu<sup>2+</sup> ions decarboxylation reactions proceeded with higher rates by a dissociative mechanism to release CO or CO<sub>2</sub> simply by heating.

## Emission Control through Catalysis

### CATL 7

#### **NO<sub>x</sub> reductions under fluid catalytic cracking conditions**

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NO<sub>x</sub> emissions contribute for acid rain, greenhouse effect and formation of ozone in the atmosphere. Because of that, environmental demands are forcing the reduction of NO<sub>x</sub> emissions in mobile and static sources. On the other hand, due to the increase of cracking of heavy feed stock, oil refineries are emitting more sulfur and nitrogen compounds. Hence, the reduction and understanding of conditions that affect NO<sub>x</sub> emissions has a great importance. This work evaluates the effect of contaminant metals in catalyst and the regeneration conditions on the NO<sub>x</sub> emission in the conditions of FCC process. Typical resid cracking catalyst containing contaminant metals were tested. Different metal levels were obtained by density separation of an equilibrium catalyst. A simulated equilibrium catalyst was also tested for comparison. NO reduction was made in typical conditions of an FCC regenerator. Partial and total combustion were simulated varying relative amount of CO and O<sub>2</sub>. NO reduction to N<sub>2</sub> varied with the type of combustion and amount of Ni and V in the catalyst. NO reduction in total combustion was very low. For partial combustion, the amount of NO reduced varied according to the amount of contaminant metals in the catalyst. This way, evaluating of NO<sub>x</sub> additives must be done taking into account catalyst regeneration condition in the unit and the amount of Ni and V in the equilibrium catalyst.

### CATL 9

#### **Partial oxidation of methane to synthesis gas over alkaline earth metal oxide supported cobalt catalysts**

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The structural properties, reducibility and reaction behaviors of alkaline earth metal oxide supported Co catalysts were investigated using X-ray diffraction, temperature programmed reduction, CO chemisorption, pulse reaction with pure methane, and catalytic partial oxidation of methane to synthesis gas. Only Co/MgO (precalcined at 1073 K) was proved to be a highly efficient and stable catalyst. It provided a CH<sub>4</sub> conversion of 91% and a CO selectivity of 98% at the high space velocity of 720000ml/g/h, without any deactivation for the duration of the experiment (120 h). A solid solution of CoO and MgO was identified in the 1073 K calcined MgO supported catalyst, which is responsible for its superior activity. Due to its low reducibility, the metal crystallites formed during the reduction of the solid solution were small and hence little carbon deposition occurred. Being formed from a solid solution, the crystallites were partially embedded into the substrate and thus were resistant to sintering. Moreover, the reactivity of Co/MgO catalysts was strongly affected by the calcination temperature and Co loading.

## Emission Control through Catalysis

### CATL 10

#### **Influence of chromium on sulfur resistance of supported Pd catalyst for aromatic hydrogenation in diesel fuel**

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In recent years, more and more attention has been paid to aromatic hydrogenation in diesel fuel because aromatics lower the fuel quality and increase the undesirable emissions from diesel engine. Noble metal catalysts exhibit high activity for aromatic hydrogenation, but such catalysts are generally sensitive to sulfur poisoning. In recent years, many works are reported on sulfur resistance of noble metal catalyst. Sulfur is a major poison to noble metal catalysts for deep aromatic hydrogenation in petroleum refining industry. To improve the sulfur resistance of such catalysts, a series of Pd, Cr, and PdCr bimetallic catalyst supported on HY/Al<sub>2</sub>O<sub>3</sub> was studied by NH<sub>3</sub>-TPD, pyridine adsorption IR, TPR, CO adsorption IR, and toluene hydrogenation in the presence of 3000 ppm sulfur as thiophene under conditions 533-573 K, 4.2 MPa, and WHSV 4.0 h<sup>-1</sup>. Cr has no influence on acidity of catalyst. TPR patterns and in-situ CO adsorption IR revealed the strong interaction of Cr and Pd, and the formation of PdCr bimetallic particles after reduction. The frequency shift of linear bonded CO on Pd indicated that electron density of Pd decreases with the increase of Cr/Pd atomic ratio. Catalytic performance of Pd, Cr and PdCr bimetallic catalysts showed that the sulfur resistance of Pd is strongly enhanced by Cr, and the activity reaches its maximum when Cr/Pd atomic ratio equals to 8. Correlations between the catalytic performance and catalyst structure, the electron-deficient palladium are responsible for the excellent sulfur resistance of PdCr bimetallic catalysts.

### CATL 11

#### **Production of hydrogen from the catalytic reformulation of methanol**

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The potential use of hydrogen powered fuel cells for transportation has obtained increasing attention in recent years due to the prospective reduction of CO<sub>2</sub> emissions and hazardous pollutants (i.e., NO<sub>x</sub>, SO<sub>x</sub>, particulates). Reformulation of methanol is an attractive possibility for the on-board generation of hydrogen in mobile fuel cell-powered systems. However, even trace amounts of CO (>20 ppm), formed from methanol decomposition, can contaminate the Pt anode of Polymer Electrolyte Membrane (PEM) fuel cells. Three reactions producing CO-free hydrogen from methanol are steam reforming, partial oxidation, and oxidative steam reforming. In this study the effectiveness of each reaction scheme in producing CO-free hydrogen over Cu/Zn-based catalysts is examined. Comparisons to Ce/Pt catalytic system are also presented. Effect of synthesis parameters on the surface and structural characteristics of the catalysts is also discussed.

### CATL 12

#### **Palladium based catalysts for the synthesis of alcohols**

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The search of catalysts able to produce alcohols from syngas is matter of a great deal of attention. It is well known the ability of palladium to produce methanol from syngas. The modifications of the normal behaviour of palladium based catalysts by supports (ZnO and ZrO<sub>2</sub>) and metals ( Ru and Fe) in the CO hydrogenation reaction has been studied. Characterisation of the catalytic systems will also be presented.

## Emission Control through Catalysis

### CATL 13

#### High-stability water-gas shift catalysts based on nanocrystalline ceria

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New low-temperature water-gas shift (WGS) catalysts are under development to produce essentially CO-free hydrogen to feed the PEM fuel cells in future automobiles. Desired catalyst characteristics include high activity and stability over a wider operating temperature window than is presently possible with the commercial shift catalysts. In this work, we present data from Cu and Au/ceria catalysts prepared by co-precipitation and gelation as highly dispersed nanostructured materials, and tested under a variety of operating conditions. The backbone of the catalyst is ceria, while the metal or metal oxide is the minor phase, 2-5 wt%. The ceria-based catalysts studied in this work contained 10 at% La. Both the Ce(La)Ox and the metal oxide/metal phases were nanocrystalline: <7 nm and < 4 nm, respectively, after air calcination for 10 h at 400oC (Au samples) or 650oC (Cu samples). These catalysts show a remarkable structural stability in WGS over a wide range of operating temperatures (150-650oC for Cu-ceria, 150-400oC for Au-ceria). Reactivity tests were conducted in a fixed-bed flow microreactor using various reaction gas compositions and space velocities in the range 8000-80,000 h<sup>-1</sup> (STP). The reaction products, CO<sub>2</sub> and H<sub>2</sub>, were included in these tests, to investigate their effect on the catalyst activity and selectivity. Steady-state WGS reaction kinetics were measured over the temperature range 175-300oC. The redox reaction model fits well the observed kinetics. H<sub>2</sub>-TPR established that the presence of copper or gold in Ce(La)Ox increases the reducibility of this material. The light-off temperature of the WGS reaction matches the onset temperature of reduction of Cu- or Au-Ce(La)Ox.

### CATL 14

#### First-principles modeling of reactions on oxide surfaces for automotive exhaust after treatment

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Lean-burn and gasoline engines offer significant fuel economy benefits over traditional stoichiometric combustion engines, but to take advantage of these benefits, new types of catalysts capable of removing NO<sub>x</sub> in an oxygen-rich exhaust are required. A promising strategy is the use of a lean NO<sub>x</sub> trap catalyst, which oxidizes and stores NO<sub>x</sub> during lean engine operation and releases and reduces the NO<sub>x</sub> to N<sub>2</sub> during periodic rich purges. Alkaline earth oxides are commonly used as the active components of NO<sub>x</sub> traps, but current realizations have unsatisfactory NO<sub>x</sub> storage capacity and are prone to poisoning by sulfur. In this work, first-principles density functional theory calculations are used to study the mechanisms of NO<sub>x</sub> and SO<sub>x</sub> adsorption and storage on representative alkaline earth oxide surfaces. The relative adsorption tendencies are compared, and the role of the oxide surface in catalyzing oxidation of adsorbates considered. The results provide valuable insights into the chemistry of oxide surfaces that are relevant not only to NO<sub>x</sub> traps but to supported catalysts in general.

## Emission Control through Catalysis

### CATL 15

#### Highly active lean NO<sub>x</sub> catalysts: Hysteresis in the presence of water

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We will describe modifications of ferrierite by a number of aqueous treatments followed by Co<sup>2+</sup> ion-exchange or gas-phase exchange that yield CoFER catalysts that reduce NO<sub>x</sub> to N<sub>2</sub> with substantially higher efficiency over a broader temperature range than typically observed. The topology of the FER framework is implicated in the broad temperature window of NO<sub>x</sub> conversion. We will describe the systematic influence of framework topology (FER, MFI, MOR, Beta) on activity of a variety of Co-zeolite catalysts. It is well-known that water in the reactant feed gas competes with NO<sub>x</sub> adsorption on microporous lean NO<sub>x</sub> catalysts at low temperatures influencing the NO<sub>x</sub> reactivity. We will describe a reversible hysteresis in catalytic activity that depends on the recent thermal history of the catalyst. These effects have significant technological implications for the application of microporous catalysts as lean NO<sub>x</sub> catalysts, and the design of new catalysts.

### CATL 17

#### Characteristics of Cu/Ti-PILC catalyst for the reduction of NO<sub>x</sub> by propene

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The selective catalytic reduction of NO<sub>x</sub> by hydrocarbon (SCR/HC) had been regarded as a promising NO<sub>x</sub> removal technology. In particular, CuZSM-5 and CuMOR catalysts exhibit high NO removal activity by hydrocarbons. However, these catalysts have not been successfully commercialized due to their weak water and sulfur tolerances. In the present study, the characteristics of Cu ion-exchanged titania pillared interlayered clay (Cu/Ti-PILC) catalyst for SCR of NO<sub>x</sub> by propene have been examined by a variety of analytic techniques including PSD, XRD, TPD, TPR and XANES. The catalytic activity varied with respect to the preparation condition of Ti-PILC and the content of Cu ions on the catalyst surface. As the content of the metal increases, the NO removal activity decreases. The TPR patterns of the catalyst were quite unique with respect to the preparation method and condition of the catalyst. It may be mainly due to the state of Cu phase on the catalyst surface. Cu/Ti-PILC catalyst exhibited stronger water tolerance than the conventional SCR/HC catalysts containing CuZSM-5 and CuMOR, since the surface of the Cu/Ti-PILC is relatively more hydrophobic than the zeolite catalysts. Cu/Ti-PILC catalyst prepared in the present study revealed superior NO removal activity to the CuZSM-5 and CuMOR catalysts, regardless of the existence of water in the feed gas stream to the reactor. This may be elucidated by the peculiar physicochemical properties of Cu-TiPILC catalyst including pore structure and surface acidity for the reduction of NO by propene.

## Emission Control through Catalysis

### CATL 18

#### **Identification of surface intermediates on palladium-based catalysts in NO<sub>x</sub> reduction with lower hydrocarbons**

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Palladium-based catalysts were synthesized through modified sol-gel chemistry and studied for catalytic reduction of NO<sub>x</sub> with lower hydrocarbons such as methane, propane, and propylene. In-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was used under both steady-state and transient conditions to identify the adsorption species. Adsorption-desorption characteristics of the catalysts were examined by temperature-programmed desorption (TPD) probe molecules. The modification of the surface in the presence of water and SO<sub>2</sub> is also investigated.

### CATL 19

#### **Low-temperature SCR of NO with NH<sub>3</sub> over water resistant transition metal oxides supported on titania**

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Titania supported Mn, Cr, and Cu catalysts were studied for low-temperature (100°-160°C) SCR of NO with NH<sub>3</sub> using a feed containing elevated levels of NO (2000 ppm each of NO and NH<sub>3</sub> and 2.0 vol% O<sub>2</sub>). For the best catalyst, 20wt.% Mn/Hombikat TiO<sub>2</sub>, quantitative performance with 100% N<sub>2</sub> selectivity was achieved at 120°C. Under wet conditions the above catalyst was found to be highly stable even in the presence of 10.0 vol.% H<sub>2</sub>O and gave over 80% NO conversion at 160°C; low (1.7 vol.% H<sub>2</sub>O) water content showed quantitative performance. Characterization by NH<sub>3</sub> FT-IR and TPD, XPS and XRD showed that the presence of Lewis acidity, controlled overall acidity and multiple metal oxide phases (redox properties), MnO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub> for example, are important parameters. Low temperature catalyst calcination (300°-400°C) helps achieve and maintain high performance even though the precursor is only partially decomposed. To whom correspondence should be addressed: panagiotis.smirniotis@UC.EDU

### CATL 20

#### **Molecular beam study of NO reduction on rhodium catalysts**

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We report on isothermal kinetic studies on the reduction of NO by CO on rhodium single-crystal surfaces using collimated effusive molecular beams. The optimum rate of reaction is achieved when the steady-state coverages of NO and CO on the surface reach the 1:1 stoichiometric ratio. The surface coverages are controlled by a synergistic balance between the composition of the gas and the surface temperature: higher temperatures tend to require higher CO:NO ratios. Under optimum conditions the surface of the catalyst is mostly covered with atomic nitrogen islands. Production of molecular nitrogen takes place preferentially at the periphery of those islands and via the formation of a N-NO intermediate. Finally, the effects of both oxygen and sulfur oxides on the catalytic performance of rhodium were probed. Oxygen inhibits the NO reduction, but not by consuming CO, rather by poisoning the adsorption of CO.

## Emission Control through Catalysis

### CATL 21

#### **Spectroscopic and theoretical insight into the mechanistic aspects of SCR reaction over vanadia-titania catalysts**

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The mechanistic aspects and the nature of the surface active sites for the Selective Catalytic Reduction (SCR) of NO<sub>x</sub> by NH<sub>3</sub> over vanadia-titania catalysts have been widely studied in the recent years. Despite the many different views on the detailed nature of the system, there is general consensus that the reaction involves either V-OH, V=O groups or both. The present Raman and FTIR spectroscopic investigations have focused on the detailed nature of these surface functional groups and the results indicate a strong surface structural dependence on temperature. In order to understand the origin of these changes, density functional theory (DFT) calculations have been carried out on different V<sub>2</sub>O<sub>5</sub> structural models. The combined results indicate that proton mobility between different sites occurs with a strong consequence for the catalysis.

### CATL 22

#### **Lean NO<sub>x</sub> catalysis for mobile source emission control**

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The desire for improved fuel economy is projected to boost the demand for diesel-fueled vehicles in the coming years. Consequently, NO<sub>x</sub> removal from lean exhaust gas by selective catalytic reduction with hydrocarbons continues to receive considerable attention. In this paper the development of precious metal-based catalysts for NO<sub>x</sub> reduction on light duty diesel trucks - aimed at LEV emission legislation - is outlined. In view of the demanding durability requirements placed on automotive catalysts, potential catalyst deactivation mechanisms are considered - including the role of sulfur - and methods of improving catalyst durability are discussed. Also considered are strategies for secondary injection of the diesel fuel reductant aimed at maximizing NO<sub>x</sub> conversion at minimum fuel penalty. Results obtained for several promising catalyst systems in engine bench and chassis dynamometer tests will be presented.

### CATL 23

#### **Poisoning effect of SO<sub>2</sub> on NO reduction by i-butane over Fe/ZSM-5 prepared by sublimation method**

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XPS, in situ EPR, FTIR, SO<sub>2</sub> TPD and reaction tests were performed to investigate the effect of SO<sub>2</sub> on NO reduction by i-butane over Fe/ZSM-5 prepared by sublimation method. Kinetic studies showed that SO<sub>2</sub> in reaction mixture poisoned Fe/ZSM-5 irreversibly. XPS after reaction with SO<sub>2</sub> at 623 K revealed the formation of sulfate species, which was corresponding to SO<sub>2</sub> TPD result. In situ EPR spectrum showed that the lines arising from distorted tetrahedral Fe<sup>3+</sup> ions at g=5.8 and 6.5, which were known to be reactive species, disappeared and a new one at g=1.9978 assigned to paramagnetic coke species appeared. The pre-adsorption of SO<sub>2</sub> suppressed the formation Fe-NO<sub>2</sub> and Fe-NO<sub>3</sub>. Based on these results, it was concluded that SO<sub>2</sub> deactivated Fe/ZSM-5 by suppressing the formation of Fe-NO<sub>2</sub> and Fe-NO<sub>3</sub> complexes and promoting the formation of carbonaceous deposits, which resulted in the consumption of the active Fe<sup>3+</sup> sites.

## Emission Control through Catalysis

### CATL 24

#### **New active zeolite structures for the selective catalytic reduction of nitrogen oxides: ITQ-7 and IM5 zeolites.**

##### **The influence of NO<sub>2</sub> on this reaction**

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Contrarily to what occurs with other gas pollutants such as SO<sub>2</sub> or CO, the NO<sub>x</sub> emissions coming mainly from automotive exhaust engines are increasing and their control becomes an urgent necessity. In the last years main attention has been paid to the use of Cu/Co-ZSM5 or Cu/Co-beta as catalysts for the selective catalytic reduction of NO in presence of oxygen but no clear explanation about the mechanism of the reaction has appeared. In this work we have studied the activity of two new zeolite structures discovered in the last two years: ITQ-7 and IM5. ITQ-7 has a pore topology formed by a tridirectional system with 12 members rings closed to the structure of beta zeolite. IM5 structure is still unknown but it is suggested that may be formed by either 10 MR crossing pores or 10 MR pores with lobes, close to the structure of ZSM5. Both present high activity for the catalytic reduction of NO<sub>x</sub>. In these catalysts, the addition of NO<sub>2</sub> to the feed stream results in an increase of the overall rate of reduction of NO<sub>x</sub> and simultaneously reduces its dependence on the oxygen concentration.

### CATL 25

#### **Study of the conversion of chlorided hydrocarbons over acid catalysts**

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The conversion of some model chlorided hydrocarbons such as 1-chloropropane, 2-chloropropane, 3-chloropropene (allylchloride), 1,2-dichloropropane and 1,3-dichloropropane over silica-alumina has been investigated on a flow reactor. Other acid catalysts such as HZSM5, WO<sub>3</sub>-based materials have also been tested.

Mechanistic studies have been performed using FT-IR spectroscopy. Kinetic evaluations, such as the measures of reaction orders and of activation energies, have also been performed. The dehydrochlorination to the corresponding olefins occurs above 450 K in all cases. This reaction occurs after a previous adsorption of the organic compound in the form of alkoxide species. Chlorine at secondary carbon atoms eliminates faster than those at the primary one. The rate determining step is an E1-type elimination of the alkoxide through carbenium ions. Double dehydrochlorination of dichloropropanes to propene also occurs at higher temperatures. 1-chloropropenes intermediates react faster than 3-chloropropene. A dehydrochlorination process can be proposed to recover chlorine as HCl from wastes and to limit their chlorine content before incineration. The experiments have been later extended to ethylenetrichloride (trielin) and 1,1,1-trichloroethane in the absence and in the presence of steam.

### CATL 26

#### **Unique materials design for catalytic emission control systems**

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Based on novel synthesis techniques certain unique materials have been recently developed which exhibit exceptional physical and catalytic properties which may yield important practical benefits as emission control catalysts.

The relation between the synthesis techniques and material properties are described and some applications are elucidated, focusing on the reduction of Sulfur emissions.

## Emission Control through Catalysis

### CATL 27

#### **Development of an active and environmentally selective bifunctional metal-zeolite catalyst for the chlorinated VOCs emissions abatement**

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Catalytic oxidation of chlorinated volatile organic compounds (CVOCs) has become an effective and economically advantageous strategy due to its low operating temperatures (300-500°C). Both activity and selectivity of three H-type zeolites (H-Y, H-ZSM-5 and H-mordenite) and two supported noble metal catalyst (0.5%Pt/Al<sub>2</sub>O<sub>3</sub> and 0.5%Pd/Al<sub>2</sub>O<sub>3</sub>) were evaluated for the 1,2-dichloroethane (DCE) and trichloroethylene (TCE) gas-phase oxidation. Comparative studies indicated that both type of catalysts showed a similar global activity in CVOCs destruction. H-type zeolites showed a slightly higher conversion in DCE decomposition whereas noble metal catalysts resulted more active in TCE decomposition. The main differences were found when analysing the reaction product selectivity. H-type zeolites showed a lower selectivity toward the formation of higher chlorinated by-products and molecular chlorine. However, noble metal catalysts were more selective to the formation of CO<sub>2</sub> instead of CO, the major product formed over H-type zeolites. As a conclusion, a highly and selective but cheaper novel catalyst can be designed by combining both supported metal catalyst and H-type zeolite properties, e.g. by adjusting catalyst acidity and metal content in the zeolite to improve both oxidation activity and selectivity to environmentally desirable products (CO<sub>2</sub>, H<sub>2</sub>O and HCl).

### CATL 28

#### **Effect of particule size on oxidation processes on platinum catalysts**

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In order to design catalysts rationally, quantitative relationships between catalyst structure and rates of elementary reactions are needed. In this study, we use density functional theory to compute rates of elementary reactions on platinum particles as a function of particle size and morphology. Reactions studied involve O, S, SO<sub>2</sub>, SO<sub>3</sub>, NO, and NO<sub>2</sub>, all relevant to automotive catalysis. We find significant variations as a function of particle size, and analyze these variations in terms of electronic orbital energy levels in order to develop rules of reactivity and selectivity.

## Emission Control through Catalysis

### CATL 29

#### Fluorine emission control of the semiconductor industry by surface wave plasma

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The new trend in the semiconductor industry has been established to be a move toward NF<sub>3</sub>-based chemistries especially in the CVD chamber cleaning process due to the reduction or elimination of PFC emission. The drawback is the increased generation of F<sub>2</sub>. Although current in-situ C<sub>2</sub>F<sub>6</sub> chamber-cleaning processes generate some F<sub>2</sub> as a by-product, NF<sub>3</sub>-based cleans can emit up to 6 times as much F<sub>2</sub> due to high NF<sub>3</sub> flows and conversion efficiencies. A non-equilibrium surface wave plasma technology is presented. This new generation plasma device can be easily integrated into various industrial applications for the abatement of F<sub>2</sub> gas. Additive water vapor is compared to additive hydrogen and oxygen gases as sources of free radical species. These free radical sources prevent the reformation of F<sub>2</sub>. Mixtures of NF<sub>3</sub> and CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> with C<sub>2</sub>H<sub>2</sub> were also studied. The fluorine balance, by-product distribution and DRE determination were accomplished by quadruple mass spectrometry and FTIR spectrometry. This plasma device is fully optimized to reduce F<sub>2</sub> gas emission by >99%.

### CATL 30

#### Catalytic oxidation of Cl-VOCs in flue gas from a waste incineration pilot plant

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It is well known how atmospheric combustion of waste and residues in fluidized bed (AFBC) is hindered by the formation of harmful dioxins and other toxic pollutants. They can be abated by catalytic reactors downstream from the waste incinerator but it is quite expensive. The main focus of this work is the catalytic hot gas clean up. Tests on catalytic total oxidation of Cl-VOCs have been made in two very different facilities: a lab scale facility using synthetic gas mixtures with targeted Cl-VOCs (CH<sub>2</sub>Cl<sub>2</sub>, chlorobenzene, C<sub>2</sub>HCl<sub>3</sub>), and a small pilot plant based on a fast fluidized bed incinerator of 15 cm i.d., 6 m high, 1-5 m/s superficial gas velocity, fed by 2-10 kg/hr. Two different feedstocks were used in this pilot plant: mixtures of (1 to 5 mm) wood chips with commercial PVC chips (total Cl content in feedstock: 1.0 wt%), and dried sewage sludge doped with several metallic salts and with PVC. Downstream from the AFBC there is a 40 mm i.d. catalytic reactor in a slip or by-pass flow. The cat. reactors used were both of stainless steel and of glass, with several thermocouples in them. They operate as a fixed bed (for spheres) and as a structured (monolithic) reactor both with space-velocities of around 5,000 h<sup>-1</sup> (n.c.). Catalysts tested include spheres, extrudates and monoliths, commercial available and new ones (under research), and noble metals (Pt and Pd based) and V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>. Samples of gas are taken (under standardized methods) before and after the catalytic reactor, at different times-on-stream, and for different temperatures in the catalytic reactor (between 200 and 450° C). Such samples are then analyzed (by GC-MS standard methods). VOCs and Cl-VOCs present in the flue gas are then identified before and after the catalytic reactor. In the pilot incinerator most commonly found VOCs were benzene, naphthalene, and as Cl-VOCs: mono, di-, tri-, tetra-, chlorobenzenes. Conversion of all these compounds are calculated for different catalysts under several space-velocities and temperatures. 99 % elimination of most of these contaminants with catalysts is often achieved. Comparison between catalysts is made regarding their activity and life span.

## Emission Control through Catalysis

### CATL 31

#### Global warming potential reduction of the industrial SF<sub>6</sub> emission by surface wave plasma

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A non equilibrium surface wave plasma technology is presented. This third generation plasma device can be easily integrated into various industrial application for the abatement of SF<sub>6</sub> gas. Additive water vapor is compared to additive hydrogen and oxygen gas as sources of free radical species. These free radical species prevent the reformation of SF<sub>6</sub>. Mixtures of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> with SF<sub>6</sub> were also studied. The by-product distribution and DRE determination were accomplished by FTIR spectrometry. This plasma device is fully optimized to reduce SF<sub>6</sub> gas by >99%.

### CATL 32

#### Thermoanalysis of threenuclear oxo-acetate cluster complexes of ferric (III) and chromium (III)

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In this report have been carried results out of studying thermoanalytical characteristics of homo- and heteronucleus m<sub>3</sub>-oxoacetates of the ferric (III) and chromium (III) composition [M<sub>3</sub>(O)O<sub>3</sub>CH<sub>3</sub>COOH] where M<sub>3</sub>=Fe<sub>3</sub>, Fe<sub>2</sub>Cr or Cr<sub>3</sub>. The thermoanalysis, chosen in hard type of complex combination, conducted in the interval of temperatures 20-10000°K using derivatorgraph Q-1500 D Paulic-Paulic-Erdiy's systems, has allowed to install that thermoliz of studied complexes proceeds in range of 40-3300°K and consists of several stages. On the base of derivatography datum and results of the chemical analysis has been conducted attributing some observed stages of thermal decomposition of complexes. Shown that the first stage of thermoliz of all four clusters can be attributed to the total losing of external sphere molecule of acetate acids and three internal sphere molecules of water. The last exothermal stage of thermal destruction brings to entire combustion of complexes using air oxygen, as a result of those stay metals oxides as a hard remainder. For the first endothermic stage have been carried calculations out of kinetic parameters and determined topochemical mechanisms of process thermoliz of studied combinations. Calculations have been realized by the method of Khorvits-Metsger with accounting of additions of Topor on the program, which we have developed. As a source has been used datum, which were received by the transformation type of analog signal ÕG in figures six channel recorder of derivatorgraph. The time interval of printing of signal ÕG assigned by impetus, controlling step engine of recorder. In the report is discussed obtained kinetic parameters of thermoliz investigated complex combinations.